

AFAL-TR-79-1234



GaAs SURFACE PASSIVATION FOR DEVICE APPLICATIONS

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JANUARY 1980

TECHNICAL REPORT AFAL-TR-79-1234
Interim Report 2 for period 15 December 1978 through 14 June 1979

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and germanium nitride; and mixtures of silicon dioxide, gallium oxide, and aluminum oxide.

Furing this report period, GaAs metal-semiconductor gate field effect transistors were evaluated for microwave gain degradation following encapsulation with a plasma-deposited dielectric. Average gain degradation at 9.70 GHz was 0.5 dB.

Evaluation of plasma-deposited 'Ge₃N₄" films indicated that substantial oxygen contamination can occur even when the deposition system is leak tight. Interactions of the plasma with the walls of the deposition chamber are believed to be responsible. Design of an improved deposition system is described.

Capacitance-voltage (C-V) data for MIS capacitors prepared using several dielectrics prepared by plasma deposition and photochemical deposition are presented. All the C-V curves are nonideal. Several phenomena observed in these C-V data are discussed.

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PREFACE

The work reported here is supported by the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under contract F33615-78-C-1444. The monitoring engineer is Capt. R.L. Johnson. The program objective is to investigate the passivation of gallium arsenide and the application of dielectric thin-film overlayers in metal-insulator-semiconductor field-effect transistors.

This work is being performed jointly by Hughes Research Laboratories and the Technology Support Division of Hughes Aircraft Company. Contributions to this work have been made by C.L. Anderson, M.D. Clark, J.W. Peters, R.A. Jullens, and F.L. Gebhart.

This is the second interim report. The first was published as AFAL-TR-79-1057 with the same title.

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INTRODUCTION AND SUMMARY

The goal of this program is to develop dielectrics that will serve the following three basic purposes in gallium arsenide device technology:

- Passivation reduction of the number of electrically active centers ("surface states") at the semiconductor surface so that the surface potential can be modulated by control electrodes ("gates") overlying the dielectric.
- Isolation insulation of control electrodes from each other and from the substrate.
- Encapsulation overcoating of operational circuits to reduce their sensitivity to environmental influences.

To serve these three purposes, Hughes Aircraft Company is developing a variety of deposited dielectrics. Techniques for depositing these dielectric materials are being developed under Hughes internal funding. Evaluation and optimization of these materials for GaAs device applications are being performed under the subject contract.

The following materials are being developed:

- $Ga_xAl_yO_z$ (gallium-aluminum oxide), referred to as $(Ga_xA1)O$
- $Ga_xSi_yO_z$ (gallium-silicon oxide), or (Ga,Si)0
- $Al_x Si_y O_z$ (gallium-silicon oxide), or (Ga,Si)0
- $Al_x Si_v O_z$ (aluminum-silicon oxide), or (Al,Si)0
- $Si0_{v}^{N}$ (silicon oxynitride)
- (Si,Ge)N (silicon-germanium nitride).

Three basic techniques for depositing these materials are being evaluated:

- Pyrolytic chemical vapor deposition (CVD)
- Plasma-enhanced deposition (PED)
- Photochemical deposition (PCD).

During this report period, an evaluation of our proprietary plasma-deposited isolation glass as an encapsulant for GaAs-microwave FETs was performed under Hughes internal funding. The average gain degradation resulting from encapsulation was only 0.5 dB at 9.7 GHz. Because of the success of this material as both an isolation glass and an encapsulant, we have shifted our emphasis toward passivation studies.

In our continuing work on the (Si,Ge)N system, physical characterization of "Ge₃N₄" films prepared by PED showed that plasma-induced desorption from the chamber walls contributes significantly to oxygen contamination in these films. Construction of a new PED system designed to reduce this and other problems has begun under Hughes internal funding.

An evaluation of the electrical interface properties of a variety of dielectrics prepared by PED and PCD was begun during this report period. PED ${\rm Si0}_{\rm X}{\rm N}_{\rm y}$ (with intentional oxygen doping) showed strong "pseudo-inversion" (i.e., a tendency for the capacitance of MIS capacitors under depletion conditions to saturate at an unexpectedly high capacitance value). PED " ${\rm Si}_3{\rm N}_4$ " and " ${\rm Ge}_3{\rm N}_4$ " exhibited stable deep depletion, a condition believed to be maintained by insulator leakage. PCD " ${\rm Si}_3{\rm N}_4$ " exhibited very flat MIS capacitance-voltage (C-V) behavior in accumulation and possible "pseudo-inversion."

ENCAPSULATION OF GaAs FETs

Using Hughes internal funding, we performed an initial study of the usefulness of our proprietary plasma-deposited isolation glass as an encapsulating material. Four microwave GaAs FETs with 1 x 600 μm gates and mounted in NEC carriers were evaluated for microwave gain at 9.70 GHz before and after deposition of the dielectric glass. The results are presented in Table 1. On the basis of the four measurements on each device, the average gain degradation resulting from encapsulation was 0.45 dB. In view of the increased parasitic capacitance resulting from the presence of the glass, we feel this reduction in gain is very reasonable. Thus, our plasma-deposited dielectric is at least superficially useful for encapsulation. As indicated in Interim Report 1, this same glass has for some time also been routinely used to isolate clock lines in all of our GaAs ICs. Because of the success of this material in isolation and passivation applications, we have shifted our emphasis on this program toward passivation, the most challenging use of dielectrics in GaAs device applications.

TABLE 1. Response of GaAs FETs to Encapsulation

Gain Change, dB	-1.15	-0.7	٠,	+0.3	-0.55	-0.25	-0.15	-0.05	6814
Gain Change dB	-1	0-	-1	9	0	0	0	0-	4
Encapsulated Gain, dB	7.1	6.9	7.75	7.6	7.4	7.3	7.4	7.3	
Unencapsulated Gain at 9.70 GHz, dB	8.25	7.6	9.05	7.3	7.95	7,55	7.55	7,35	
Input Power, dBm	0	+10	0	+10	0	+10	0	+10	
Drain Current, mA	50	06	50	06	50	06	90	06	
Drain Bias, V	2.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	
Gate Bias, V	-3.05	-1.62	-2.91	-1.56	-3.42	-2.02	-3.5	-1.96	
Device No.	1		2		e		7		

PHYSICAL PROPERTIES OF " Ge_3N_4 " FILMS PREPARED BY PED

The initial films of "Ge $_3$ N $_4$ " prepared by PED (and described in AFAL-TR-79-1057) were found to be both germanium rich and oxygen contaminated. The best composition achieved was \sim 77 at.% Ge, 19 at.% O, 4 at.% N. Part of the oxygen contamination was traced to a vacuum leak in the system. Films prepared after the leak had been repaired, however, still exhibited substantial oxygen contamination. Thus, the oxygen contamination appears to result only partially from vacuum leaks.

Additional oxygen apparently results from the action of the plasma on the surface within the deposition chamber, as a result of sputtering, heating, or optically excited desorption. The observed dependence of the dielectric constant of the films on rf power is taken as evidence of this desorption effect. Three " Ge_3N_4 " depositions were performed with constant gas flow conditions (10 sccm of 1.5% GeH_4 in Ar; 40 sccm of N_2) at a constant substrate temperature of 200°C. The rf power was varied from run to run. Films deposited with an rf power of 28 W exhibited an index of refraction (as measured by ellipsometry with 6328-A-wavelength light) of 1.87, whereas films prepared at rf powers of 70 and 300 W exhibited indices of 1.78 and 1.47, respectively. Amorphous pyrolytic Ge_3N_4 exhibits an index of 2.06, while amorphous GeO_2 has an index of about 1.6. Thus, the variation of the refractive index of our PED "Ge $_{3}N_{\mu}$ " films is assumed to result from oxygen contamination that increases with rf power. Density changes may also be a contributing factor. Similar variations are seen for "Si $_3\mathrm{N}_4$ " prepared by PEO.

These considerations indicate why higher N_2 flow rates are not notably effective in reducing oxygen contamination. Higher flow rates without corresponding increases in pumping speed result in higher chamber pressures and therefore require higher rf powers to maintain stable discharges.

The quality of the PED films prepared for this contract should significantly improve when construction of the new PED system shown

in Figure 1 is completed. This system is being built using Hughes internal funding. We believe that the design of this system is significantly better than that of the present system (described in AFAL-TR-79-1057). In the new system, the reducing gases (silane, germane, etc.) are introduced through a side port, rather than through a tube passing down the axis on the rf coil. This arrangement reduces the amount of surface area in the most intensely excited region of the plasma and precludes the possibility of a plasma being generated within the delivery tube for the reducing gases.

The dispersal ring for the reducing gases is attached to a bellows assembly and is capable of oscillating in both horizontal axes over the heater assembly. The heater assembly itself is capable of rotation. We believe that the use of these mechanical motions will result in very uniform deposition over large areas. The sample holder assembly is 16 cm in diameter and is capable of holding four 5-cm-diameter circular wafers.

The sample holder itself is a plate that can be lifted off the heater using a lifting ring controlled by a push-pull/rotary feedthrough and removed from the system through an access door (not shown) in the front of the chamber. During pumpdown, the sample holder can be positioned away from the heater to maintain a low sample temperature. Once high-vacuum conditions are achieved, the samples can be rapidly heated to deposition temperature by placing the sample holder plate onto the heater assembly. This provision reduces the possibility of baking contaminants onto the sample surface prior to deposition.

A mechanical shutter is provided to permit covering the sample during any "preburn" procedure used to outgas the chamber before deposition. The central chamber itself is a large sphere to reduce outgassing of the walls resulting from the proximity to the heater assembly.

During a typical deposition cycle, the system will be evacuated to high vacuum conditions ($<10^{-5}$ mm Hg, or 10^{-3} Pa) before reactive gases are introduced. The diffusion pump will then be valved off and the actual depositions performed under evacuation by a large-capacity rotary

pump protected by a vacuum particle filter. All gas flow rates will be controlled by mass flow controllers. Deposition pressure will be monitored by two capacitance manometer absolute pressure gauges. Because the accuracy of these gauges degrades after numerous depositions, a reference gauge which is valved off during deposition cycles has been provided. It will be used to calibrate the "working" gauge prior to each day's runs.

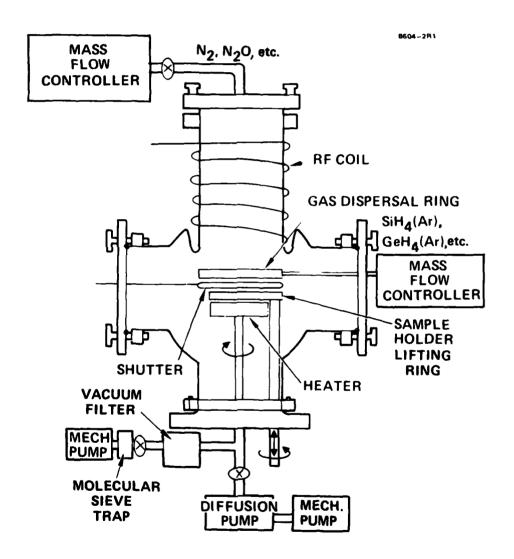


Figure 1. Schematic of improved plasma-enhanced-deposition (PED) system.

ELECTRICAL CHARACTERIZATIONS OF PED AND PCD FILMS

During this report period, we performed ac C-V analysis on MIS capacitors incorporating a variety of dielectrics. These dielectrics included silicon oxynitride (SiO $_{\rm X}$ N $_{\rm y}$) intentionally doped with oxygen and prepared from silane, nitrogen, and nitrous oxide by PED; PED "Si $_3$ N $_4$ " prepared from silane and nitrogen; PED "Si $_3$ N $_4$ " prepared from silane, nitrogen, and hydrogen; PED "Ge $_3$ N $_4$ " prepared from germane and nitrogen; and PCD "Si $_3$ N $_4$ " prepared from silane and ammonia.

Representative C-V characteristics are presented in Figures 2 through 8. Data on the fabrication process and sample parameters are provided with each figure. Insulator thicknesses were determined by Tolansky interferometry alone or in conjunction with ellipsometry using 6328-Å light.

All the C-V characteristics exhibit substantial hysteresis and frequency dispersion, which preclude any meaningful quantitative analysis of surface-state densities. There are, however, qualitative differences between the characteristics of the various dielectrics. One form of behavior that varies dramatically in its intensity between the various films is "pseudo-inversion." If we take the insulator capacitance C_i to be the maximum observed capacitance (as would be the case if strong accumulation is obtained), then we can calculate the inversion capacitance $C_{\mbox{inv}}$ from the doping density in the substrate. Under the bias polarity that tends to produce depletion, some samples exhibit a region of essentially constant capacitance at a capacitance considerably greater than C over a substantial range of bias voltages. We call this phenomenon, which is evidently the result of a high density of surface states, "pseudo-inversion," This phenomenon is clearly evident in the case of the PED Sio_{x}^{N} over " Si_{3}^{N} " samples, as shown in Figure 2.

In the case of the PED " $\rm Si_3N_4$ " samples (Figures 3 and 4), a steady-state capacitance lower than $\rm C_{inv}$ can be achieved, indicating that a stable deep depletion condition can be achieved. Such a situation can be

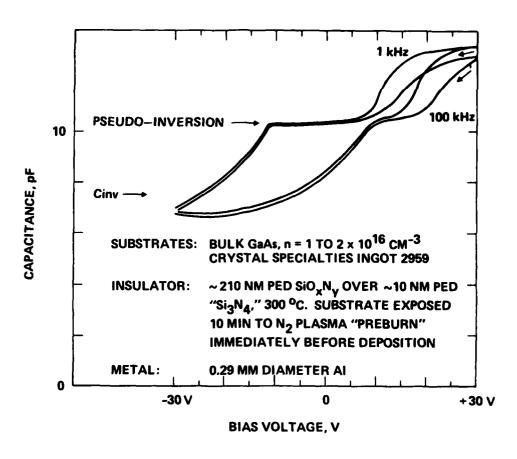


Figure 2. C-V behavior of an MIS capacitor incorporating a PED SiO N over PED "Si $_3$ N $_4$ " dielectric.

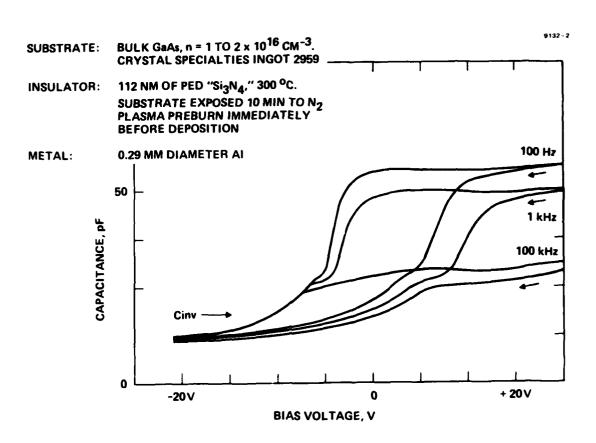


Figure 3. C-V behavior of an MIS capacitor incorporating a PED "Si $_3$ N $_4$ " dielectric prepared from silane and nitrogen.



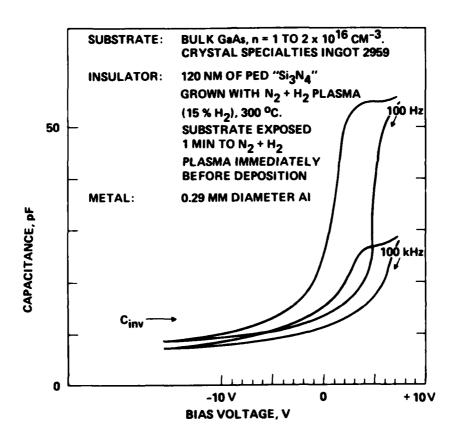


Figure 4. C-V behavior of an MIS capacitor incorporating a PED "Si₃N₄" dielectric prepared from silane, nitrogen, and hydrogen.

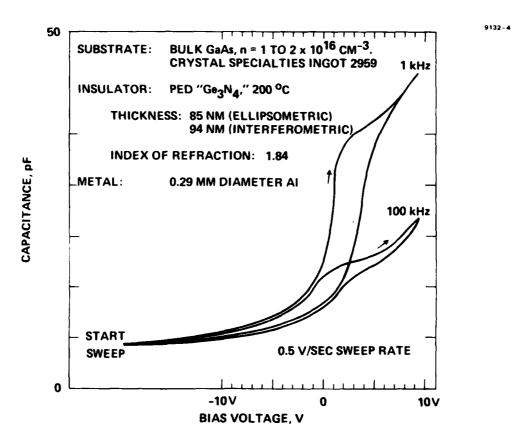


Figure 5. C-V behavior of an MIS capacitor incorporating a PED "Ge $_3\mathrm{N}_4$ " dielectric.

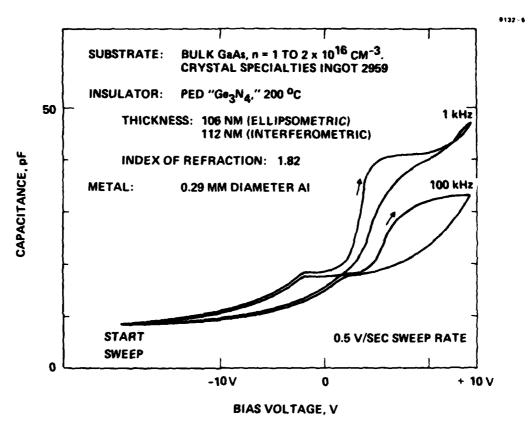


Figure 6. C-V behavior of an MIS capacitor incorporating a PED $^{\prime\prime}\text{Ge}_3\text{N}_4^{\prime\prime}$ dieletric.

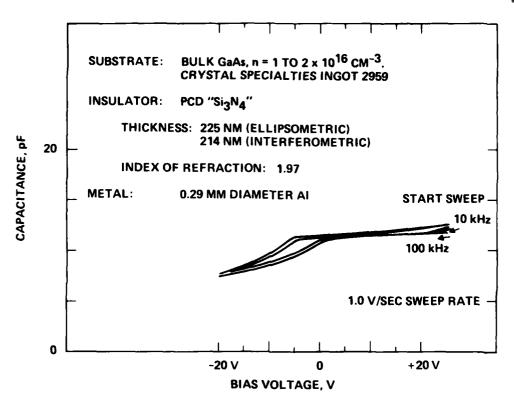


Figure 7. C-V behavior of an MIS capacitor incorporating a photochemically deposited "Si $_3\mathrm{N}_4$ " dielectric.

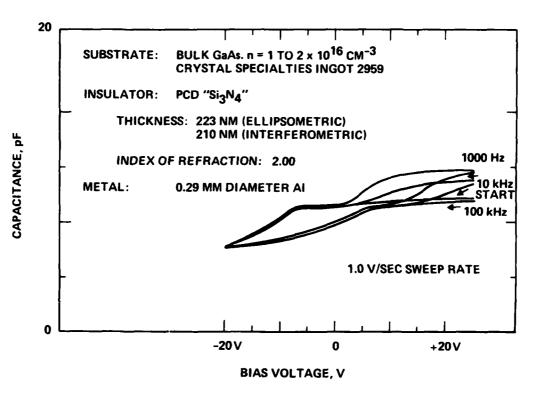


Figure 8. C-V behavior of an MIS capacitor incorporating a photophotochemically deposited "Si $_3$ N $_4$ " dielectric annealed at 400°C in forming gas.

maintained only if minority carriers are prevented from accumulating at the insulator-semiconductor interface. The "Si $_3$ N $_4$ " is considerably more conductive than the SiO $_x$ N $_y$. Inversion may be prevented by the conduction of holes through the nitride layer. The relative weakness of "pseudo-inversion" in the nitride samples indicates that either the surface state density configuration is different or that conduction through the insulator is affecting the surface state occupancy.

Dielectric constants deduced for the PED SiO $_x$ N $_y$ and PED "Si $_3$ N $_4$ " prepared without hydrogen are 5.1 ε_o and 8.5 ε_o , respectively. The measured C $_i$ and thickness values for the PED "Si $_3$ N $_4$ " grown with added hydrogen imply a dielectric constant of 11.1 ε_o , suggesting that the film is probably Si rich.

C-V characteristics for two PED " $\mathrm{Ge_3N_4}$ " films are presented in Figures 5 and 6. The " $\mathrm{Ge_3N_4}$ " films exhibit sufficient conductance to prevent measuring the C-V behavior under accumulation biases at 100 Hz. Significant frequency dispersion occurs, but the hysteresis in these films is moderate compared to the PED " $\mathrm{Si_3N_4}$ " films. Deep depletion without evidence of inversion is observed. This may be due to the presence of conduction through the dielectric.

The PCD "Si $_3$ N $_4$ " films (Figures 7 and 8) exhibit very weak voltage dependence of the C-V characteristic under accumulation bias conditions. Only minor improvements in their C-V behavior were obtained following 400°C anneal in forming gas. The C-V curves for both PCD "Si $_3$ N $_4$ " films exhibit flat regions near zero bias that appear to represent "pseudo-inversion." Thus, it appears that the surface state densities in these films are high.

IMPROVEMENTS IN ANALYTICAL CAPABILITIES

A Gaertner L116 Automatic Ellipsometer operating at 6328 $\mathring{\text{A}}$ optical wavelength was acquired during this reporting period. It has been used for film thickness and refractive index measurements and will also be used for characterizing substrate cleaning procedures.

A Hewlett-Packard 4275A variable frequency (10 kHz to 10 MHz) LCR meter has been ordered and will be installed in our calculator-based data acquisition system to perform computer-controlled C-V characterization of films prepared for this contract.

